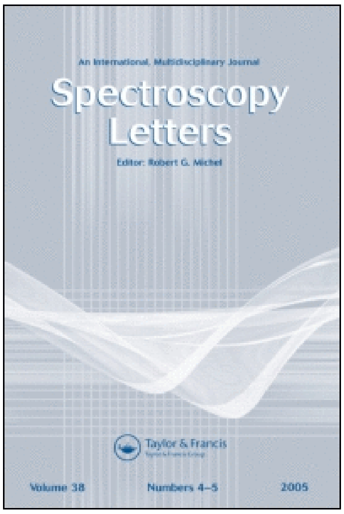

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FORMATION OF HgX(B-STATE) DUE TO HgX_2/CH_3HgX (X=Cl, Br, I) AND $N_2(A)$ COLLISIONS

Key Words: Mercury Halide Lasers, HgX_2 and CH_3HgX (X= Cl, Br I), $N_2(A)$, $N_2(B)$, $N_2(C)$ states, Emission, Atomic lines, Molecular Bands, Rate Constants, Efficiency.

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ABSTRACT

Relative rate of HgX(B-State) formation due to collisions involving HgX_2 or CH_3HgX (X= Cl, Br, I) and $N_2(A)$ has been measured in a microwave discharge pumped NaN_3 vapors. These rates are $K_1 : K_2 : K_3 : = 1 : 6.4 : 8.6$ and $1 : 4.8 : 7.7$ in case of $HgX_2 + N_2(A)$ and $CH_3HgX + N_2(A)$ collisions respectively. The K_1, K_2, and K_3 are the rates corresponding to Cl, Br, and I containing compounds.

INTRODUCTION AND BACKGROUND:

There has been a considerable interest in improving the efficiency of mercury halide lasers observed due to electrical discharge pumping of HgX_2 vapors (X= Cl, Br, I). Improved performance of these lasers has been observed by introducing a small amount of inert gases such as N_2 and Xe [1]. This is due to the fact that a large number of metastable state N_2(A) and Xe(^{3}P) are generated in the discharge medium and the HgX(B-state) is produced due to collisional dissociation of excited HgX_2 (b $^{1,3}\Sigma$) into HgX and X atoms (X= Cl, Br, I). In addition to the formation of these excited state species, a large number of ionized species [2] such as HgX_2^+, HgX^+, X_2^+, X^+, N_2^+, N^+ and Xe^+ etc. are also expected to be produced due to either direct electron impact ionization of the neutral species such as HgX_2, HgX, X_2, N_2, and Xe etc. or collisional fragmentation of the ionized species already present in the discharge medium due to collisions of the energetic electrons. It is to be noted here that the excited state species such as HgX(B), N_2(A) and Xe(^{3}P) are expected to have very high rate of electron impact ionization, mainly because of their reduced ionization potentials. For N_2(A), the electron impact ionization cross-section at 20 eV has been measured to be about $5x10^{-17}$ cm^2 [3]. The loss of the parent ie. HgX_2 (X= Cl, Br, I) and active species ie. N_2(A) and Xe(^{3}P) may be minimized by introducing a small amount of alkali-vapors, especially Na-vapors, in the discharge medium. Because of the low ionization potential of the atomic sodium, its melting point and vapor pressures comparable to the HgX_2-salts, efficient production of Na(3p)-level and its well studied discharge properties [4], it may be used in a discharge medium along with the HgX_2-vapors to generate mercury halide lasers. By minimizing some of these loss processes mentioned earlier in the presence of the Na-vapors, the efficiency of the HgX(B-X) transition lasers may be improved. For example, the reactions $HgBr_2^+$ + Na(3p) --- $HgBr_2^*$ (b, $^{1,3}\Sigma$) + Na^+ and N_2^+ + Na(3p) ---- N_2 (C-State) + Na^+ are exothermic by 1.42 and 1.2 eV respectively. The $HgBr_2^*$ ($^{1,3}\Sigma$) being in a repulsive state will dissociate into HgBr(B) + Br. The N_2 (C-State), which has a very short radiative life time (58 nsec.) will terminate to the N_2(B-State) and populate the N_2(A-State) during the N_2(B) -- N_2(A) transition. The charge transfer reactions involving $HgCl_2^+$ and HgI_2^+ with Na(3p) leading to the formation of HgCl(B) and HgI(B) states are exothermic by 1.48 and 0.95 eV respectively. We have recently studied the discharge properties of NaN_3 and have observed intense atomic sodium lines and band systems due to N_2(C-B), N_2(B-A) and N_2(A-X) transitions [5].

In this communication, we report our results on the relative rate of formation of HgX(B-state) radicals due to collisions involving HgX_2 or CH_3HgX with N_2(A) generated by microwave discharge pumped NaN_3 vapors.

EXPERIMENTAL PROCEDURE:

A schematic diagram of the apparatus used in the present study is shown in Fig. 1., details of which has been reported elsewhere [5], and only a brief description will be given here. The discharge system was made of quartz tubing of 11mm diameter and was attached with two small bulbs for loading NaN_3 and HgX_2 or CH_3HgX salts, when needed. The NaN_3 and HgX_2 or CH_3HgX crystals were heated by heating tapes and the temperatures were measured by using a digital thermometer. The discharge tube was evacuated by a mechanical pump with pumping speed of 30 CFM. With this pump it was possible to achieve pressure in the range of 10^{-4} Torr in less than half hour. A tuned Evanson cavity powered by a microwave generator was used to initiate the discharge. At NaN_3 temperatures (150 to 280 C) and forward microwave power of (30-70 W) with minimum reflected power, strong emission spectrum of the sodium lines and N_2(C-B), N_2(B-A) and N_2(A-X) band systems were observed and recorded at about 20 cm away from the discharge region. These spectra were recorded in the absence of CH_3HgX or HgX_2 vapors. When a small amounts of HgX_2 or CH_3HgX vapors were introduced into the system as shown in Fig. 1, emission spectra due to HgX(B-X) transition and mercury atomic lines were observed. The emission spectrum was dispersed by using a 0.2m monochromator equipped with 2400 groove/mm grating and interfaced

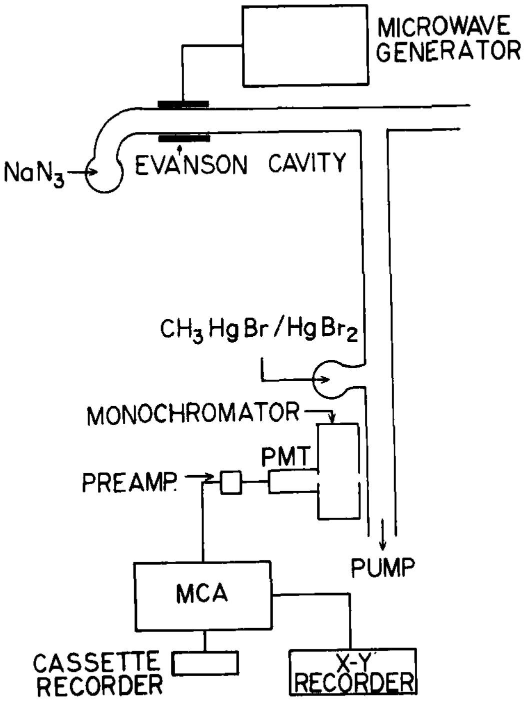

Fig. 1. Experimental set-up used in the present study.

with a scanner and detected by a cooled photomultiplier (PMT) operating in counting mode. The amplified output of the PMT was fed to a multichannel analyzer (MCA) or to an X-Y chart recorder. The MCA was interfaced with a digital cassette tape recorder for storing and plotting data on an Epson model LX-80 printer.

The reagents ie. HgX_2 and CH_3HgX (X= Cl, Br, I) were purchased from Alfa Chemical Comp. with stated purity of 95% and were used without further purification.

RESULTS AND DISCUSSIONS

The observation of the N_2(C-B) and N_2(A-X) band system about 20 cm away from the discharge region is mainly due to the energy pooling

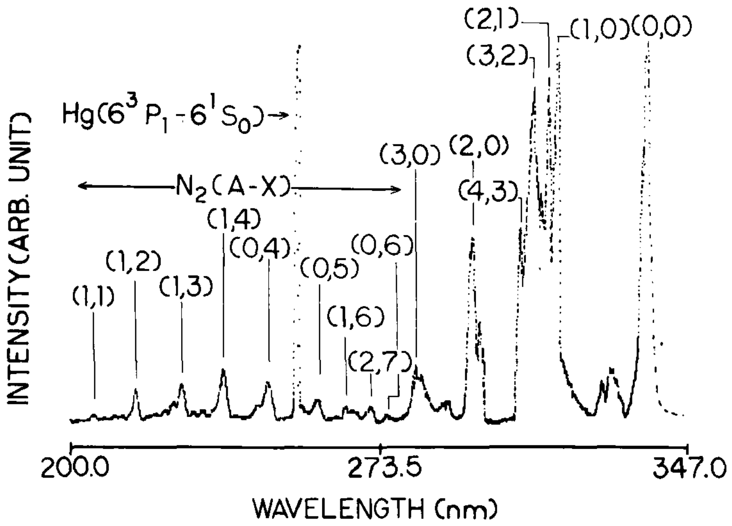

Fig. 2. Partial emission spectrum of N_2(A-X) and N_2(C-B) band systems. The spectra are uncorrected for the optical detection efficiency.

processes involving N_2(A) + N_2(A) collisions. The rate of formation of N_2(C) and N_2(B) states [6] due to this process is known to be 2.6 $\times10^{-10}$ and 1.1×10^{-9} cm^3 sec^{-1} $molecule^{-1}$ respectively. In Fig.2, we display a partial emission spectrum of the N_2(A-X) and N_2(C-B) band systems. The observation of the sodium atomic lines, as mentioned above is due to the energy transfer process [7] N_2(A) + Na(3s) ----- Na** + N_2(X), where Na** represents highly excited states of atomic sodium. The emission cross sections of Na(3p) and other highly excited states range from 100 to 200×10^{-16} cm^2. The emission spectrum of HgX(B-X) band system along with some mercury atomic lines were observed due to collisions of HgX_2 and N_2(A) and is shown in Fig. 3. The observation of the HgX(B-X) band system is a direct consequence of excitation of the HgX_2 to the repulsive state [8] HgX_2(b, $^{1,3}\Sigma$) and subsequent dissociation into HgX(B) + X atoms. It is worth noting here that the reaction $HgCl_2$(X) + N_2(A, v=1)---- HgCl(B) + Cl + N_2(X) is endothermic by 0.05 eV [5], where $HgCl_2$(X) and N_2(X) are the ground state species. An inspection of Fig.2 clearly shows that excited levels as high as v=3 of N_2(A) has been observed in the

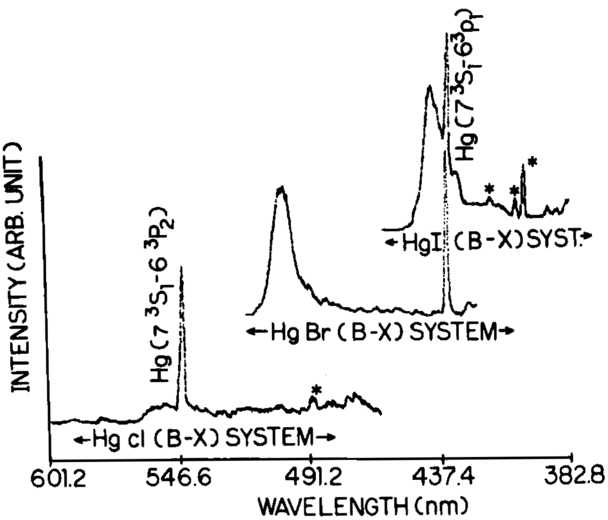

Fig. 3. Emission spectra of the (B-X) band system of HgCl, HgBr and HgI radicals and mercury atomic lines. The spectra are uncorrected for the optical detection efficiency.

present study. Under these conditions, the above reaction becomes exothermic by 0.4 eV and HgCl(B) state is possible. The emission bands due to the HgCl(B-X) transition is shown in Fig. 3. When HgX_2 was replaced by CH_3HgX (X= Cl, Br, I) under similar conditions and heated to about 40C, emission spectra of the HgX(B-X) band system and mercury atomic lines were observed as before with HgX_2-vapors. However, in this case emission spectra due to CH(A-X) and CN(B-X) transitions were also observed. The observation of the CH(A-X) bands is probably due to the collisional dissociation of the CH_3HgX molecules. But the observation of the CN(B-X) bands may be due to the recombination processes involving CH(A) + N --- CN(B) + H, which is highly exothermic. The observation of the emissions from the highly excited states of mercury is due to collisional dissociation of HgX_2 and CH_3HgX vapors and subsequent energy transfer from N_2(A) and N_2(B) states, as has been explained in our earlier publication [5] in case of CH_3HgX and HgX_2 molecules. The HgX(B-X) emission spectrum is expected to be due to the dominant process N_2(A) + HgX_2/HgX(X) ---- HgX(B) + X + N_2(X). However, charge transfer processes, as mentioned earlier may also partially contribute to the HgX(B-state) formation. The ions such as N_2^+ and N^+ may be produced in discharge region [9] and generate HgX_2^+, HgX^+ and Hg^+ ions during the charge transfer process. The ionization potentials [10] of N_2, and N are 15.5 and 14.58 eV respectively whereas these potentials for the ground state HgX_2, HgX and Hg are 11.5, 10.88, 10.19 eV, 12.06, 11.83, 10.88 eV and 10.43 eV respectively with X= Cl, Br, I. These ions when react with Na(3p) will lead to the formation of the HgX(B-state) as explained earlier. By measuring the integrated intensities of the HgX(B-X) transition, we have determined the relative rate of HgX(B-state) formation due to the collisions involving HgX_2 or CH_3HgX and $N_2(A)$ and other processes, if any. There are two important factors in determining these rates. These are the number densities of the collision partners and the absolute detection efficiency of the optical system at a particular wavelength. Our optical system was calibrated by using a standard lamp traceable to NBS and rechecked by measuring the electron-impact excitation cross sections of sodium atomic lines at 10 eV. These cross sections were found to be in reasonable agreement with those reported by Phelps and Lin(4). The temperature of HgX_2 was maintained at 100C and the vapor density was calculated by using the thermochemical data reported in reference [11]. To our knowledge, there is no experimental or theoretical density data reported for CH_3HgX molecules at different temperatures. According to Dreilling and Sester [12], the densities of HgX_2 and CH_3HgX at 100C and 35C respectively are about the same within the experimental error of 30%. We, therefore, maintained the temperature of CH_3HgX at 35C. The flowing vapors of NaN_3 were generated at 280C and passed through the Evanson Cavity tuned at 70W of forward microwave power. Thus the densities of the neutral and ionized species, if any, were constant through out the experiments. These informations when substituted in the radiative decay rate formula $I= K [N_2(A)] [HgX_2]$, where I, $[N_2(A)]$, and $[HgX_2]$ are the integrated intensity corrected for the optical efficiency, rate constant, and densities of $N_2(A)$ and HgX_2 respectively. For simplicity, we have ignored the minor contribution of charge transfer reaction to the formation of HgX(B-state). As indicated earlier that the NaN_3 temperature and microwave power were kept constant through out all the experiments, the number density of $N_2(A)$ and charged species, if any, is expected to be constant. Therefore, the rate constant K in the above formula is directly proportional to the ratio of of the integrated intensities and the respective densities of HgX_2 (X= Cl, Br, I). We have determined this ratio in each case separately. By doing so, the relative rate of HgX(B-state) formation was found to be $K_1 : K_2 : K_3 : = 1: 6.4 : 8.6$ where K_1, K_2 and K_3 are the rate constants corresponding to HgX_2 (X= Cl, Br, I) and $N_2(A)$ collisions respectively. Similarly this ratio was found to be $K_1 : K_2 : K_3 = 1: 4.8 : 7.7$ for CH_3HgX and $N_2(A)$ collisions. It is to be noted here that the densities of CH_3HgX used here have an uncertainty of 30% and therefore the relative rates of HgX(B-state) formation due to CH_3HgX and $N_2(A)$ collisions should be accurate to within 30%.

In conclusion, we have determined the relative rate of formation of HgX(B-state) during the collisions involving the metastable $N_2(A)$ and HgX_2 and CH_3HgX molecules (X= Cl, Br, I). Based on these values, it is clear that the efficiency of HgX(B-state) formation with HgX_2 and $N_2(A)$ collisions is much higher than those with CH_3HgX and $N_2(A)$ collisions. These informations may be useful in determining the relative laser efficiencies by using these molecules in a laser medium.

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